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Coupled Iron Cycling in Clay Minerals and Transformation of Petroleum Hydrocarbons across Redox Interfaces

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Fe-bearing clay minerals and petroleum hydrocarbons commonly coexist in subsurface environments such as oil reservoirs and geothermal systems. However, how the redox cycling of structural iron in clay minerals continuously drives the transformation of petroleum compounds remains poorly understood. Here, we integrate microbial cultivation, geochemical analyses, and theoretical calculations to unravel a process whereby nontronite (NAu-2) structural iron orchestrates the sequential transformation of petroleum hydrocarbons under dynamic redox conditions.

In the presence of *Shewanella putrefaciens*, crude oil hydrocarbons served as electron donors for microbial reduction of structural Fe(III) in NAu-2. The saturates supported Fe(III) reduction to an extent of 21.5%, whereas the two-ring aromatics alone achieved 30.8%—significantly higher than bulk oil (22.8%). Furthermore, the aromatics enhanced Fe(III) bioreduction when lactate was present, demonstrating its dual function as both electron donor and electron shuttle. During this process, short-chain n-alkanes and less-methylated aromatics were preferentially degraded, generating oxygen-containing compounds including fatty acids and phenols.

The biogenic Fe(II)-rich clay formed above, upon exposure to oxygen, generated hydroxyl radicals (•OH) via Fenton reactions. These •OH abiotically oxidized residual petroleum compounds through hydrogen abstraction and radical adduct formation, followed by dehydrogenation, hydroxylation, and carboxylation. Although the aromatics minimally affected Fe(II) oxidation rates, it enhanced •OH production by forming environmentally persistent free radicals, thereby amplifying the oxidative transformation. This process substantially increased the abundance of oxygen-containing polar compounds in the residual oil.

The abiotically oxidized, more bioavailable hydrocarbons were then returned to anaerobic conditions, where they stimulated Fe(III) bioreduction by a thermophilic microbial community enriched from a hot spring. Metagenomic analysis revealed that, compared to exposure to original petroleum, the pre-oxidized hydrocarbons enriched populations of *Sphingomonas* and *Phyllobacterium*—both possessing genes for anaerobic hydrocarbon activation and Fe(III) reduction—and upregulated metabolic pathways for processing oxygenated compounds.

Our findings establish a conceptual framework wherein the redox cycling of iron in clay minerals couples three interconnected processes: (1) Fe(III) bio-reduction drives initial petroleum oxidation, (2) abiotic Fe(II) oxidation generates •OH that transforms petroleum, and (3) the resulting bioavailable compounds reshape microbial community to sustain continued iron cycling. This iron-mediated "chemical-biological cascade" fundamentally links C-Fe cycles in redox-dynamic subsurface environments.